Review Article

IJCRR
Section: Healthcare
Sci. Journal Impact Factor 4.016

UTILIZATION OF AGRICULTURAL WASTE FOR BIOETHANOL PRODUCTION- A REVIEW

Nwosu-Obieogu K.[1], Chiemenem L.I.[1], Adekunle K.F.[1]

[1]Chemical Engineering Department, Michael Okpara University of Agriculture, Umudike, Abia State, India.

ABSTRACT

The utilization of agricultural waste to produce bioethanol proves to be an alternative energy source for the limited non renewable energy and a dependable substitute for food crops. Though the process has several challenges and limitations such as biomass transport and handling, efficient pre-treatment methods, high cost based on current technologies which results in low yield and high cost of the hydrolysis process. This review highlights different classes of agricultural waste, their sources and the processes undergone to produce bioethanol economically.

Key Words: Agricultural waste, Bioethanol, Pre-treatment, Lignocelluloses materials, Energy crop

INTRODUCTION

Energy is one of the most important factors to global prosperity, in view of continuously rising petroleum costs and dependence upon fossil fuel resources, considerable attention has been focused on alternative energy resources, hence the production of liquid biofuels which has been advocated as a sustainable option to tackle the problems associated with rising crude oil prices, global warming and diminishing petroleum reserves.

Bioethanol produced from renewable biomass has received considerable attention in current years; it is one means to reduce fossil fuel use and emissions of greenhouse gases. Using ethanol as a gasoline fuel additive as well as transportation fuel helps to alleviate global warming and environmental pollution. It is a high octane number biofuel which is produced from fermentation of corn, potatoes, grain (wheat, barley and rye), sugar beet, sugar cane and vegetable residues. [1-3]

In the last decade, most researchers tend to focus on developing an economical and ecofriendly ethanol production process. Much emphasis is being given to the production of ethanol from agricultural and forestry residues and other forms of biomass since they are most abundant and renewable resources on earth, which makes them attractive for production of ethanol.

Fermentation of sugar-based raw materials is referred to as "first generation" bioethanol, whereas the use of lignocelluloses raw materials is commonly called "second generation" bioethanol. The "third generation" of algal bioethanol is at an early stage of investigation. Further the cellulosic plant material represents an as–of–yet untapped source of fermentable sugars for significant use, especially non-food agricultural waste products like wheat straw, rice straw, baggasse, rice husk etc. Hence, second generation ethanol is derived from lignocellulosic materials. In these waste products, the polysaccharides, cellulose and hemicellulose are intimately associated with lignin in the plant cell wall. The lignin component acts as a physical barrier and must be removed to make the carbohydrates available for further transformation processes. Bioconversion of cellulosic biomass into fermentable sugar, for production of ethanol using microorganisms, especially cellulose degrading fungi, makes bioethanol production economic, environmental friendly and also renewable. [1, 4, 5]

Hence, the main objective of this work is to harness the potentials of agricultural waste for the production of bioethanol rather than energy crops. [1]

Agricultural Waste

Agricultural waste consists of plant biomass wastes (cellulose, hemicelluloses and lignin) grouped into different categories such as wood residues, grasses, waste paper, agricultural residues and food industries [6-8]

Corresponding Author:
Nwosu-Obieogu K., Chemical Engineering Department, Michael Okpara University of Agriculture, Umudike, Abia State.
Tel: +2348037998008; E-mail: kenenwosuobie@yahoo.com

Received: 10.06.2016 **Revised:** 13.07.2016 **Accepted:** 16.08.2016

Taherzadeh J. M. et al [9] opined that in addition to inorganic wastes, different types of polymers such as polyesters and polypropylene are available in various waste materials.

Researchers are more concerned in the production of bioethanol from wastes rather than energy crops because the latter competes for land and water with food crops to produce biofuel. Due to rise in food prices, energy crops are been discouraged from its use to produce biofuels due to current world wide rise in food prices, to resolve this conflict, it is necessary to integrate all kinds of biowaste into a biomass economy [10], though, it is mostly wasted in the form of pre-harvest and post-harvest agricultural handling in the food processing industries, due to its abundance and renewability, there has been a great deal of interest in utilizing lignocellulosic waste for the production and recovery of many value-added products [11-13]

Classification of Agricultural Wastes

Nibedita et al [14] pointed out some major agro wastes as the most favourable feed stocks for bioethanol production due to their availability throughout the year especially wheat straw and corn stover which is produced mainly at Asia and North America respectively. Lignocellulosic materials are renewable, low cost and are abundantly available. It includes Agricultural residues (wheat straw, corn Stover), municipal solid waste and forestry woody feedstock etc.

Wheat Straw

Among the agricultural residues, wheat straw is the largest biomass feedstock in Europe. About 21% of the world's food depends on the wheat crop. Hence, wheat straw would serve as a great potential feedstock for production of ethanol in 21st century. Like other biomass that has lignocellulosic constituents, it is composed of lignin, hemicellulose and cellulose. [15, 16]

Corn Stover

This is what remains on the ground after maize has been harvested. This raw material is abundantly available and demands no further investment in biomass, although not all of the corn Stover can be removed - 30% of it must be left on the ground to prevent erosion (by facilitating water infiltration and reducing evaporation), and as the main source of soil organic carbon (SOC) in order to preserve the soil's productivity. Corn Stover contains polymeric hemicellulose and cellulose, but their biodegradability by glycosidase is strongly inhibited by a small quantity (12-15%) of lignin. [15, 16]

Municipal Solid Waste (MSW)

Bioethanol production from food and vegetable industries is regarded more than other waste, for instance, fruit peels like orange, mango, banana, pineapple etc. Depending on a particular area determines the kind of waste generated, hence major waste in municipal areas consists of fruit waste, gardening waste, synthetic polymers, metals etc. [17, 18]

Forestry Woody Feed Stock

Fast growing short rotation forest trees can play an important role as feedstock for bioenergy production. However, forest is unevenly distributed. Forest play important environmental role in preservation of marginal land and reducing CO_2 levels in the atmosphere. Forest woody feedstock account for approximately 370 million tons per year of lignocellulosic biomass in the US [20], other countries rich in forest are for example, Canada, the Russian Federation, Brazil, and China. Together, these countries account for more than half of the total forest area worldwide. Sources of woody materials include residues left in natural forest, forestry wastes, such as sawdust from sawmills, wood chips and branches from dead trees, and cultivated short rotation energy forest plantations utilizing several fast growing tree species. There are two types of woody materials, softwoods, or hardwoods. Softwoods originate from conifers and gymnosperm trees.

Unlike hardwoods, softwoods possess lower densities and grow faster. These trees comprise of evergreen species such as pine, cedar, spruce, cypress, fire, hemlock, and redwood. Hardwoods are mainly found in the Northern hemisphere and include trees such as poplar, willow, oak, cottonwood, and aspen. In the US, hardwood species account for over 40 % of the trees. An advantage of woody biomass over agricultural plants is the flexibility in harvesting times as they do not depend on seasonality. Trees also contain less ash compared to crops and are of higher density, due to the thick secondary wall, which makes their transportation more economical [19-21].

Conversion of Agricultural Waste to Ethanol

In the last two decades, many researchers have worked on the conversion of lignocellulosic materials to ethanol extensively and came up with the conversion processes which include [22-24].

Hydrolysis of Cellulose in the Lignocellulosic Materials

Cellulose can be hydrolysed using acid hydrolysis which is a traditional method and enzymatic hydrolysis (the current state of art method). Enzymatic hydrolysis is preferred to acid hydrolysis because it runs at a lower temperature, higher conversion and environmentally friendly, hence most recent research has focused on it.

The hydrolysis is usually catalyzed by cellulase enzymes, cellulase enzyme depolymerize cellulose into fermentable sugars, cellulase synthesized by fungi and bacteria work together to degrade cellulose [25].

Fermentation of Suger to Ethanol

The best known microorganisms for ethanol production from hexoses are the yeast Sacchamyces cerevisiae and the bacterium Zymomonas mobilis offering high ethanol yields (90–97% of the theoretical) and high ethanol tolerance up to ca. 10% (w/v) in fermentation medium [26,27].

Pretreatment Technologies for Agricultural Waste

Within the context of production of fuels from biomass, pretreatment has come to interpret processes by which cellulosic biomass is made subsidiary to the action of hydrolytic enzymes. All naturally occurring, and most refined, cellulosic materials require pretreatment to become accessible to the enzymes that mediate hydrolysis. Typically, hydrolysis yields in the absence of pretreatment are less than 20% of theoretical yields, whereas yields after pretreatment often exceed 90% of theoretical. The limited effectiveness of current enzymatic processes on softwoods is thought to be due to the relative difficulty of pretreating these materials. [28]

Pretreatment must meet the following requirements:

- Destroy lignin shell protecting cellulose and hemicellulose
- Decrease crystallinity of cellulose
- Increase porosity
- Must break this shell for enzyme to access substrate (sugar) [28].

Pretreatments are roughly classified into physical, chemical and biological processes.

Physical Pretreatment

The first step in using wheat straw for ethanol production is size reduction through milling, grinding or chipping which can improve the efficiency of downstream processing. However, use of very small particles may not be desirable due to higher energy consumption in milling stage as well as imposing negative effect on the subsequent pretreatment method. Initial and ultimate particle size, moisture content and material properties are among variables that influence both energy consumption and the effectiveness of subsequent processing [29].

Physico-Chemical Pretreatment

Liquid hot water (LHW), steam explosion (SE) and ammonia fiber explosion (AFEX) are among physico-chemical methods investigated for pretreatment of wheat straw further illustrated below

Type- Steam-explosion

Conditions-Pressure= 2.5-7 MPa. Temperature=180-280oC

Advantages

- Well known and already used
- high yields
- no corrosion problems
- undesired side products possible

Disadvantages

- High energy demand

Type-Liquid Hot Water

Condition-Temperature= 170-230^{o}C

Advantages

- High yields
- Less side products than in steam explosion
- No corrosion problems

Type-CO_2 Explosion

Condition-Pressure is greater than 7.3 MPa. Temperature is greater than 31.1^{o}C.

Advantages

- Low environmental impact
- Disadvantages
- High cost expected

Type- Ammonia Fibre Explosion

Conditions - Temperature- 90-100^{o}C

Advantages

- Media recoverable
- Low inhibitor formation

Disadvantages

- Environmental issues due to ammonia [29,30]

Chemical Pretreatment

Chemical pretreatment for agricultural waste employ different chemicals such as acids, alkalis, and oxidizing agents e.g. peroxide and ozone. Among these methods, dilute acid pretreatment using H_2SO_4 is the most-widely used method. Depending on the type of chemical used, pretreatment could have different effects on lignocellulose structural components. Alkaline pretreatment, ozonolysis, peroxide and wet oxidation pretreatments are more effective in lignin removal whereas dilute acid pretreatment is more efficient in hemicellulose solubilization. Acid hydrolysis using inorganic acids such as H_2SO_4 have been used for pretreatment of agriculture waste to improve downstream enzymatic hydrolysis. Alkaline process is based on utilization of dilute bases in pretreatment of lignocellulosic feedstock. Using ooxidizing agents in Alkaline/oxidative pretreatment an oxidizing compound such as hydrogen peroxide (H_2O_2) or peracetic acid ($C_2H_4O_3$) is used in combination with an alkaline (e.g. NaOH) and it is usually carried out under mild temperature. This treatment is more effective in improving of crop residue digestibility compared with NaOH treatment alone. In Ozonolysis, ozone

is used to solubilise lignin and a small fraction of hemi- Cellulose from wheat straw. [31]

Biological Pretreatment

Biological pretreatment comprises of using microorganisms such as brown-, white-, and soft-rot fungi for selective degradation of lignin and hemicellulose among which white-rot fungi seems to be the most effective microorganism.

The pretreatment types are illustrated further-

Pretreatment Type- fungi treatment wit fungi

Organisms Involved-white rot fungi, brown rot fungi, soft rot fungi

Advantages

- No chemicals required
- Mild environment conditions
- Low energy requirements

Disadvantages

Slow conversion

Pretreatment Type- bacteria

Organism Involved- Sphingomonas paucimobilis, Baillus circulans

Advantages

- No Chemicals Required
- Mild Environment Conditions
- Low Energy Requirements

Disadvantages

- Slow conversion [30]

Challenges

Currently researchers are looking for possible alternative fuels from cheap sources like agricultural wastes, this is faced with serious challenge, it is easier to produce bioethanol from energy crops, but it is not economically viable since the energy crops are consumed as food, during pre-treatment process, some inhibitory compounds like weak acids from derivatives and phenolic compounds inhibits the subsequent process of saccharification and fermentation. These compounds are yield limiting which ultimately affects the cost of whole process and now become a big challenge.

This high price is because of some technological impediments encountered in all different steps of the process. Pretreatment is estimated to account for 33% of the total cost. The current leading pretreatment methods for lignocellulosic materials are capital intensive, also maintaining a stable performance of the genetically engineered yeasts in commercial scale fermentation operations, developing more efficient pretreatment technologies for lignocellulosic biomass, and integrating the optimal components into economic ethanol production systems.

Also on report, that global demand for food and for transportation fuels is expected to increase more than 50 times, so there is a great need for renewable energy supplies that do not compete with food supply. Biofuels produced from agricultural residues such as underutilized cellulosic materials are likely to be more useful and economical feasible [19].

Hence it is very important to control the production of these compounds, review the cost of the pretreatment process and encourage the use of agricultural waste. [32]

CONCLUSION

It has been proven that conversion of agricultural wastes to bioethanol has paved way for underutilised resources and encouraged environmental sustainability, hence ethanol-from-cellulose (EFC) holds great potential due to the widespread availability, abundance, and relatively low cost of cellulosic materials biomass resources, nevertheless biological pretreatments should be encouraged because it is safe, environmentally friendly and less energy intensive compared to other pretreatment methods.

ACKNOWLEDGEMENT

Authors acknowledge the immense help received from the scholars whose articles are cited and included in references of this manuscript. The authors are also grateful to authors/ editors/publishers of all those articles, journals and books from where the literature for this article has been reviewed and discussed.

REFERENCES

1. Koshy, J., Nambisan, P. (2012) Pretreatment of Agricultural waste with *pleurotus sp* for ethanol production. *International journal of plant, animal, and enviromental sciences*. 2 :2
2. Icoz, E., Mehmet Tugrul, K., Saral, A. (2008) Research on ethanol production and use from sugar beet in Turkey. *Biomass and Bioenergy.* 10 (1016).
3. Graboski, M.S. (2002) Fossile energy used in the manufacture of corn ethanol prepared for natural corn growers association pp 14-17.
4. Patel, S., Onkarappa,r., Shobha,k. (2006) Study of ethanol production from fungal retreated wheat and rice straw. *The Internet Journal of Microbiology*. 4 (1)
5. Kang, Q., Appels, L., Tan, T., Dewil, R. (2004) Bioethanol from Lignocellulosicbiomass :current findings determines research priorités. *Hindawi publishing coorpration.* The scientific world journal 2014 :1-13

6. Qi BC, Aldrich C, Lorenzen L, Wolfaardt GW (2005). Acidogenic fermentation of lignocellulosic substrate with activated sludge. *Chem. Eng. Communications*, 192(9): 1221-1242. doi:10.1080/009864490515676.
7. Roig A, Cayuela ML, Sánchez-Monedero MA (2006). An overview on olive mill wastes and their valorisation methods. *Waste Manag*. 26(9):960-969. 0.1016/
8. Rodríguez G, Lama A, Rodríguez R, Jiménez A, Guilléna R, Fernández-Bolaños J (2008). Olive stone an attractive source of bioactive and valuable compounds. *Bioreasour. Technol*. 99(13): 5261-5269. doi: 10.1016/j.biortech.2007.11.027.
9. Taherzadeh J.M and Karimi K. (2008) Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: *A Review Int. J. Mol. Sci.*, *9*, 1621-1651; DOI: 10.3390/ijms9091621.
10. Mahro B, Timm M (2007). Potential of Biowaste from the Food Industryas a Biomass Resource. *Eng. Life Sci*. 7: 457-468. doi:10.1002/elsc.200620206.
11. Pandey P, Pandey AK (2002). Production of cellulase-free thermostable xylanases by an isolated strain of *Aspergillus Niger* PPI, utilizing various lignocellulosic wastes *World J. Microbiol. Biotechnol.* 18(3):281-283. doi: 10.1023/A:1014999728406.
12. Das H, Singh S (2004). Useful by-products from cellulosic wastes of agriculture and food industry - *A critical appraisal. Crit. Rev. Food Sci. Nutr*. 44(2): 77-89 DOI: 10.1080/10408690490424630
13. Foyle T, Jennings L Mulcahy P (2007). Compositional analysis of lignocellulosic materials: Evaluation of methods used for sugar analysis of waste paper and straw. *Bioresour. Technol.* 98(16): 3026-3036. doi:10.1016/j.biortech.2006.10.013.
14. Nibedita Sarkar, Sumanta Kumar Ghosh, Satarupa Bannerjee,Kaustav Aikat (2012). Bioethanol producction from agricultural wastes : An overview. *J Renewable Energy* Vol. 37 (1) : 19-27
15. Talebnia, F., Karakashev, D., Angelidaki, L (2009) Prodcution of bioethanol from wheat straw : and overview on pretreatment, hydrolysis and fermentation*. Bioresources technology* 101(2010) :4744-4753.
16. Naik, S.N, Goud, V.V., Rout, P. K, Dalai, A.K. (2010) Production of first and second generation biofuel : a comprehensive review. *Renewable and sustainable energy review*. 14 : 578-597.
17. Beede DN, Bloom DE (1995) Economics of the generation and management of MSW. NBER working Papers 5116. *National Bureau of Economic Research, Inc*
18. Jefferson Hopewell, Robert Dvorak and Edward Kosior (2009) Plastic recycling: challenges and opportunities, *Philos Trans Soc Lond B Biol Sci; 364(1526): 2115-2126.*
19. Seguim A (2011) How could forest trees play an important role as feedstock for bioenergy production. *Curr Opin Environ Sustain* 3:090–094.
20. Perlack RD, Wright L, Turhollow LA, Graham RL, Stokes B, Erbach DC (2005) Biomasses feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. *Oak Ridge National Laboratory Report* ORNL/TM-2005/66.Oak Ridge, TN:US Dept. of Energy.
21. Sanchez OJ, Cardona CA (2008) Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresour Technol* 99:5270–5295.
22. Alriksson B, Cavka A, Jönsson LJ (2011). Improving the fermentability of enzymatic hydrolysates of lignocellulose through chemical in-situ detoxification with reducing agents. *Bioresource Technol* ;10:1254-1263.
23. Wright, J.D., (1998). Ethanol from biomass by enzymatic hydrolysis. *Chem. Eng. Prog.* 84 (8), 62–74.
24. Pérez J, Muñoz-Dorado J, de la Rubia T, Martínez J (2002). Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. *J. Int. Microbiol.* 5(2): 53-63. doi: 10.1007/s10123-002-0062-3.
25. McMillan, J.D., (1994). Pretreatment of lignocellulosic biomass. In: Himmel, M.E., Baker, J.O., Overend, R.P. (Eds.), Enzymatic Conversion of Biomass for Fuels Production. *American Chemical Society, Washington*, DC, pp. 292–324.
26. Hill, J., Nelson, E., Tilman, D., Polasky, S.,and Tiffany, D.,(2006) Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proc Nat Acad Sci*.103:11206–11210.
27. Snehal, I., Sanket, J. J, and Akshaya, G., (2014). Production of bioethanol using agricultural waste: Banana pseudo stem, *Braz J Microbiol.* 2014; 45(3): 885–892.
28. Shahabaldin, R., Mohd Fadhil, M. D., Shaza E. M., Hesam, K.,and Farzaneh S. M., (2012). A bioethanol from cellulosic materials. *International conference on environment* .
29. Saini, J.K, Saini, R., Tewari, L (2015) Lignocellulosic agriculture wastes and biomass feedstocks for second generation bioethanol production : concepts and recent development. 3 *Biotech*. 5 : 337-353.
30. Maha Dakar Challenges of Ethanol production from Lignocellulosic Biomass. *Katzen International, Inc. Technology and Engineering*
31. Talebnia, F., Karakashev, D., Angelidaki, L (2009) Prodcution of bioethanol from wheat straw : and overview on pretreatment, hydrolysis and fermentation. *Bioresources technology* 101:4744-4753
32. Umar Asghar, Muhammad Irfan, Muhammad Nadeem, Rubina Nelofer, Quratulain Syed (2015) Challenges in bioethanol production from lignocellulosic waste Energy. *Education Science and Technology Part C: Future Energy Resources* Volume (issues) 7(1): 7-16.